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Abstract. The study is aimed at the technology development of treating drinking water from ground waters with high manganese content and oxidizability. Current technologies, physical/chemical mechanisms and factors affecting in ground treatment efficiency are reviewed. Research has been conducted on manganese compound removal from ground waters with high manganese content (5 ppm) and oxidizability. The studies were carried out on granular sorbent industrial ODM-2F filters (0.7–1.5 mm fraction). It was determined that conventional reagent oxidization technologies followed by filtration do not allow us to obtain the manganese content below 0.1 ppm when treating ground waters with high oxidizability. The innovative oxidation-based manganese removal technology with continuous introduction of reaction catalytic agent is suggested. This technology is effective in alkalization up to pH 8.8–9. Potassium permanganate was used as a catalytic agent, sodium hypochlorite was an oxidizer and cauistic soda served an alkalifying agent.

1. Introduction

Almost all ground water treatment plants operate on the conventional "aeration-filtration" scheme (simplified aeration). However, plants' long-time operating experience has shown that the basic aeration treatment technology followed by light granular sorbent filtration fails to provide quality target water in terms of manganese ions [1]. Reducing the manganese content by means of conventional treatment methods takes place under increased pH values, significant excess of iron over manganese and oxidation not more than 3 mgO_2/l [1]. Currently, the issue of high oxidizability in ground treatment employing reagent methods is insufficiently explored and remains valid.

In ground treatment in noncentralised water supply environment can be realized by means of development, research and adoption of up-to-date high-performance water treatment technology employing reliable small water purification units [1, 2]. Hence, the following trends are considered urgent nowadays: development and application of supplementary techniques in order to enhance manganese removal processes; search for optimal doses and reagent combinations; and research of modern catalytic material properties [3].

The Paper presents the studies conducted on in ground treatment using granular sorbent industrial ODM-2F filters; the fraction was 0.7–1.5 mm, the bed depth equaled 1 m and filter velocity was 10m/hr. Reagents were introduced directly to filter system.

2. Physical/chemical characteristics of manganese state in ground waters

Soluble manganese content in oxygen-deficient underground and surface waters of the Sverdlovsk region reaches 5 ppm [4]. Russian sanitary norms restrict maximum admissible manganese content

in domestic water up to 0.1 ppm, while in some European countries this value is allowed to be lower than 0.05 ppm. The excess of manganese content deteriorates organoleptic properties of water. Manganese being higher than 0.1 ppm causes spots on sanitary wares and a film on pipelines. The latter is peeled off in the form of dark sediment [5].

Manganese in ground waters is presented as ion Mn^{2+}, salts of which are soluble. To remove manganese from water one should transfer it to insoluble state by oxidizing Mn^{2+} to Mn^{3+} and Mn^{4+}. Oxidized manganese compounds are cleaved with the formation of practically insoluble hydroxides $Mn(OH)_3$ and $Mn(OH)_4$. The latter when precipitated through crushed diatomaceous rock (granular sorbent) exhibits catalytic properties, i.e. accelerates Mn^{2+} oxidation process by dissolved oxygen [6].

As compared to air-oxidized ferrous bicarbonate whose pH value equals seven, manganese oxidizes within the range of high pH values and oxidation-reduction potentials. Optimum oxidation value for manganese bicarbonate oxidation is pH = 10. The lower pH values can only be kept by applying stronger oxidizing agents (chlorine, ozone, etc.) with their high excess in the reaction [7].

In addition, manganese is generally found in ground waters together with ferrous iron, but it is the iron that is removed from water utilizing the basic aeration treatment technology. Due to strong oxidizing agents, manganese oxidizes and sorbs only after iron since the latter is an easily oxidizable element. Therefore, joined purification of iron and manganese on the same stage at filter plants is feasible provided their concentration equals minimum values up to 2–5 ppm and strong oxidizing agents are employed.

Sanitary norms [8] on manganese removal directly in deferrization without adding reagents are outdated and fail to meet present requirements of the processes described. Application of various schemes to purify water from manganese or iron or both depends on contaminant concentration, plant capacity and local conditions.

3. Experimental investigation

Ground waters of the Sverdlovsk region are mainly polluted by manganese, although it is non-typical in some cases when the content of manganese exceeds that of iron.

The research of manganese removal in the city Verkhnaya Pyshma conducted by the Department of Water Management and Technology in Ural Federal University proved the concentration of manganese to be 4.5 ppm, ferrum – 0.6 ppm, silicon – 17 ppm, oxidizability – 5.5 mgO_2/l and pH = 6.8. According to the suggested reagent purification scheme, corresponding reagents were added into water, then it was immediately filtered through light granular sorbent at 10 m/hr. Preliminary research showed that mixing such water with oxygen or chlorine combined with alkalization regardless of the reagent dose did not lead to manganese retention.

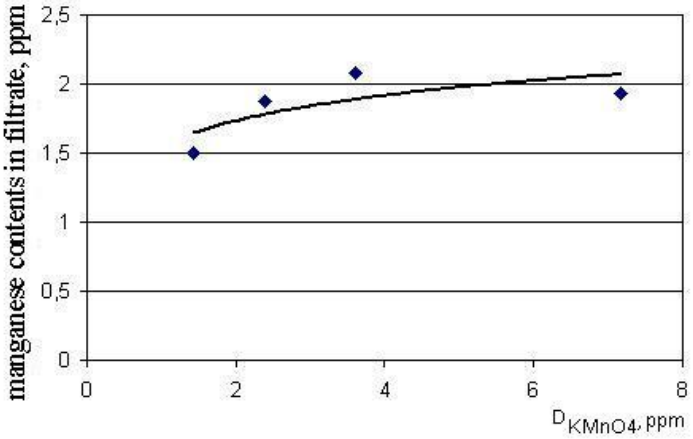

Figure 1. Dependence of manganese concentration on potassium permanganate dose (pH = 6.8) in filtrate

Then, tests were carried out to oxidize manganese with potassium permanganate followed by filtration and the results are presented in Figure 1. Introducing even low doses of potassium permanganate reduced the concentration of manganese in filtrate up to 1.5–2 ppm. However, the purification efficiency was not affected by the increase of the dose. This results from permanganate being used for oxidation of organic matters. Once the concentration of potassium permanganate is higher than 20 ppm, sharp increase of manganese content in filtrate occurs because of permanganate migration to filtrate. Given contact time of high dose of reagent with water is increased in the following filtration, the water of drinking quality is likely to be obtained by means of such process. This proves the occurrence of additional processing operation and the necessity to mount the reactor prior to fast filter.

For manganese to oxidize effectively, the pH value of water to be purified should be 8.0–8.5 [2]. Previous experiment was repeated but water was additionally alkalified with caustic soda with pH up to 8.5. The results are presented in Figure 2.

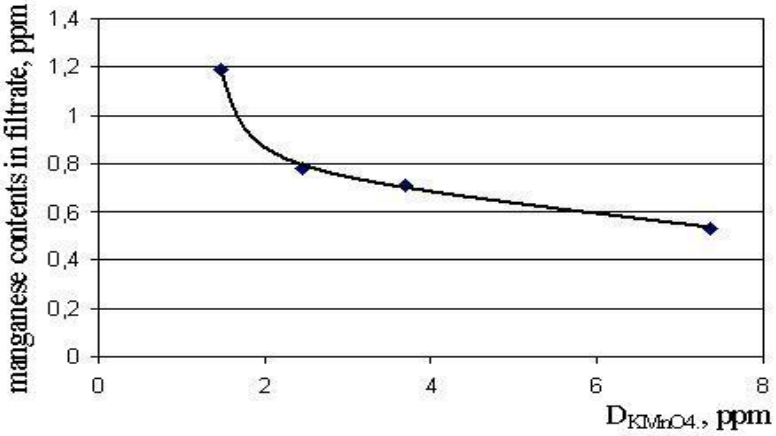

Figure 2. Dependence of manganese concentration on potassium permanganate dose (pH = 8.5) in filtrate

As shown in Figure 2 the increase of potassium permanganate dose results in the decrease of manganese content in filtrate. However, the dependence is not linear; the higher the dose, the slower the growth of the purification efficiency.

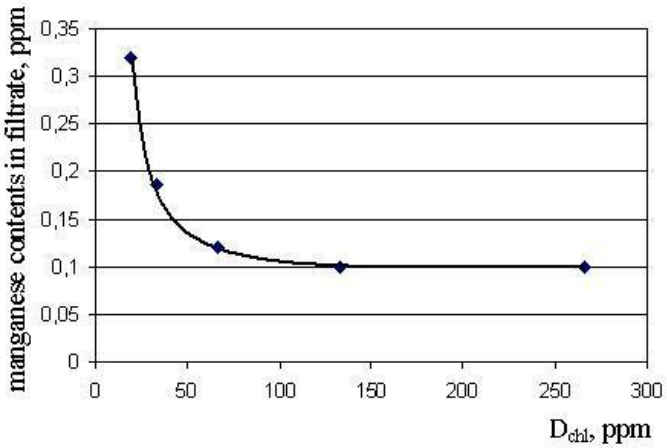

Figure 3. Dependence of manganese concentration on available chlorine dose (pH = 8.5) in filtrate

While filtering water mixed with potassium permanganate, the sorbent was modified: its granules were covered with the layer of manganese hydroxide performing several functions simultaneously – being an oxidation reaction catalytic agent, oxidizing manganese and sorbing organic compounds. Water was purified in such modified sorbent; meanwhile the oxidizing agent (sodium hypochlorite) and the alkalifying agent (cauistic soda) were added into water. Figure 3 shows the results of the experiment.

On the graph one can see that manganese is removed to meet drinking sanitary norms when chlorine dose is higher than 100 ppm in modified sorbent. Residual chlorine accounts for 80 ppm necessitating additional processing operation on its removal. In addition, organic matters and silicon compounds causing progressive decrease of purification efficiency gradually contaminate the catalytic layer (the layer of manganese hydroxide on a granule surface).

4. Technological guidelines

To avoid shortcomings of the above-listed processes, the manganese removal technology based on the application of granular sorbent with renovating catalytic layer was developed. The technology implies adding into water alkalifying and oxidizing (sodium hypochlorite) agents. Besides potassium permanganate constantly added to water accounts for 2–5 ppm. Potassium permanganate reacts instantly with manganese and organic matters creating insoluble suspension of manganese hydroxide – catalytic agent of manganese oxidation reaction. Sorbent is constantly modified by new doses of catalytic agent. In such sorbent, the contaminated catalytic agent tends to be covered with a new film of manganese hydroxide enabling oxidizing soluble manganese even with low amount of available chlorine. The sorbent should be regenerated every 6 hours by backwash as the growing catalytic layer is squeezed out to filtrate.

Based on this technology the manganese removal plant with the capacity of 300 m^3 per day was created in Verkhnaya Pyshma. Potassium permanganate available dose accounted for 3 ppm, chlorine dose was 5 ppm. Manganese concentration after purification was less than 0.005 ppm. The operation of the plant for a year has proved the reliability and efficiency of the suggested technology.

5. Conclusions

Having studied the manganese removal from ground waters with high oxidizability and manganese content (about 5 ppm), we found that the conventional oxygen or chlorine treatment of such waters even in alkaline environment fails to remove manganese irrespective of the oxidizing agent doze. Introducing insignificant doses of potassium permanganate reduces by half the manganese content in filtrate when precipitated through crushed diatomaceous rock (granular sorbent) due to the modification of the sorbent's surface. Given that, manganese hydroxide is used as the oxidation reaction catalytic agent and the dissolved organic compound sorbent. However, the introduction of potassium permanganate alone to serve as an oxidizer fails to decrease manganese in filtrate to the level required by Sanitary Regulations and Norms [8]. The pH value of water to be purified should account for 8.0–8.5, the potassium permanganate dose has to be 2–5 ppm and that of sodium hypochlorite is limited to 5 ppm for manganese to oxidize effectively. We developed the oxidation-based manganese removal technology with continuous introduction of a reaction catalytic. The ground treatment catalytic is potassium permanganate, while sodium hypochlorite serves as the principal oxidizing agent. As compared to conventional technologies (oxidation with oxygen or/and potassium permanganate followed by filtration), the technology discussed allows reducing oxidizability being above 5 mgO_2/l and manganese content accounting for 4 ppm in source water to meet the requirement of Sanitary Regulations and Norms [8].

This innovated technology tested on actual ground waters of the Ural region proved to be highly efficient for manganese removal since the concentration of manganese after purification did not exceed 0.005 ppm, thus confirming to the requirements for quality standard drinking water in the Russian Federation.

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